

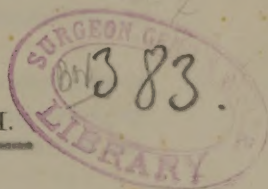
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CONSTITUTION  
OF  
ORGANIC COMPOUNDS;

BEING

A BRIEF ACCOUNT OF THE DIFFERENT THEORIES ADVANCED  
ON THIS SUBJECT.

BY PROF. HENRY ERNI.



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# CONSTITUTION

OF

## ORGANIC COMPOUNDS.

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ORGANIC CHEMISTRY embraces an almost endless number of bodies, the formation of which we must ascribe to the influence of a peculiar modification of the molecular forces; better known under the name of *vital force*.

The constituents of organic compounds are comparatively very limited, and consist principally of carbon, hydrogen, oxygen, nitrogen, and occasionally of phosphorus and sulphur.

In the first period of this now so extensive department of science, organic bodies were considered to be products of a peculiar organic force, since their formation could not be explained according to purely chemical laws: consequently, no distinction was made between proximate and ultimate constituents, and the atoms of the different elements were considered as simply joined to one another, their arrangement not being influenced by chemical attraction. The vital force formed here the cloak which concealed ignorance, and retarded the development of Organic Chemistry, like that of some other branches of natural science; since, by giving an apparently satisfactory explanation, it prevented, for a long time, further investigations. But, when philosophers recognized this force in its manifestations to be only a complication

of modified molecular forces, the difference between organic and inorganic bodies was at once greatly diminished.

Berzelius, whose sound and accurate researches enriched every branch of science, was the first who spoke thus: "The application of that which is known, and will be, of the mode of combination of the elements in inorganic nature, must be the guide by means of which we may hope to get a true and harmonious conception of the composition of those bodies which are formed under the influence of the vital process." Such a proposition — to compare inorganic nature with, and to apply its laws to, organic bodies — at once created the idea that the latter likewise consist of proximate and ultimate parts. The discovery of organic compounds of equal percentage-composition and atomic weight, but endowed with different physical and chemical properties, rendered this argument still more conclusive. We must, then, necessarily seek in their different internal composition an explanation of this fact. To these so called isomeric compounds belong, for instance, many of the essential oils of the formula  $C_{20}H_{16}$ ; further, tartaric and racemic acid, both of the formula,  $= C_4H_2O_6$ .

By looking for the proximate constituents of organic bodies or radicals in general, we meet with many difficulties. Organic compounds can rarely be prepared directly by artificial means: their composition, consequently, cannot be investigated synthetically, but simply by way of analysis. The analysis of organic bodies comprises, 1, the ultimate analysis, by means of which we find the exact relative quantity of the elements combined in an organic substance, and from that the relative number of atoms of its constituents; 2, the determination of the atomic weight, which gives us the absolute number of atoms. The execution of these two operations makes us acquainted with the empirical formula of a body. The empirical formula for alcohol is, for instance,  $= C_4H_6O_2$ , which gives us no further indication how these twelve single atoms are arranged among each other. In order to obtain the rational formula, which presents to us more closely the



inner constitution of a compound, we have to decompose it by various means and ways, and to study the relations of these products to the original substance. Alcohol, *e.g.*, may be converted into ether by simply depriving it of water. The formula of ether is known to be  $C_4H_{10}O$ ; and we may, therefore, consider  $C_4H_9O + HO$  the formula for alcohol.  $C_4H_9O$  is found, on further investigation, to bear a close analogy to an inorganic oxide, in which  $C_4H_9$ , or ethyl, represents the radical or electro-positive atom. According to these considerations, we imagine the rational formula of alcohol to be  $C_4H_9 + O + HO$ ; i.e., the hydrate of the oxide of ethyl.

The establishment of rational formula from the products of decomposition of organized bodies has, however, also given rise to many extravagant and unsustainable views. Persoz, *e.g.* adopted for acetic acid ( $C_4H_4O_4$ ) the formula  $C_2H_3 + CO + CO_2 + HO$ ; and dissected most organic acids in this manner, by presuming in them the existence of ready-formed water, carbonic acid, and carbonic oxide.

All organic bodies are, with few exceptions, easily decomposed: the slightest disturbance of the equilibrium of the chemical forces is often sufficient to recall the original affinities between the elements. The products of decomposition must vary with the different destructive agencies we employ. It is also obvious, that, from these products, different views respecting the constitution of an organic substance may be adopted, all more or less capable of accounting for the phenomena of decomposition.

Of all the theories advanced concerning the constitution of organic bodies, the so called "Radical Theory" — the development of which we will follow here somewhat in detail — alone is founded on the established laws of inorganic chemistry, and appears to be, more than any other, in accordance with experience. This theory is still, up to this day, the predominating one among chemists, particularly in Germany.

Berzelius first advanced this theory, after the publication

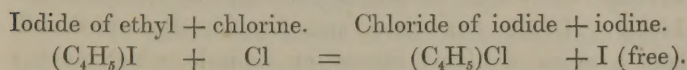
of the investigations on alcohol and ether by Gay Lussac and Dumas. He then assumed that organic bodies containing oxygen were oxides of organic radicals. By applying this view to ether, it becomes the oxide of an organic radical, capable of combining with acids like an inorganic oxide; and this analogy with inorganic compounds justifies the conclusion that compounds of Se, Te, S, Cl, Br, with this radical, could be prepared. Liebig, whose attention was called to this subject, persuaded himself of the correctness of this theory, applied it at once to the compound ethers, and named the radical ( $C_4H_5$ ) of ether, ethyl, and considered alcohol as an hydrated oxide of ethyl ( $C_4H_5$ )O+HO. He predicted, at the time, the future isolation of the radical  $C_4H_5$ . On this occasion ensued a critical discussion with Dumas, who considered ether to be the hydrate of etherine,  $C_4H_4+aq$ ; but, in consequence of a mutual exchange of opinions, Dumas altered his view, and became a zealous advocate of the radical theory. Soon after, he declared, in a note to the Academy of Sciences in Paris in his and Liebig's name, the difficult question respecting the constitution of organic bodies solved; exhibited the radical theory as the only possible one; and stated further, that, for the future, his object would be to discover and study those radicals.

Berzelius, in pointing out the direction which had to be pursued for that purpose, declared that the laws after which organic compositions take place could best be studied from the products of the metamorphosis of organic bodies, when those latter were exposed to different temperatures. Hereby, without the influence of what has been called vital force, new compounds are formed, many of which are the same produced by vitality.

The theory of organic radicals considers organic substances as consisting of compound bodies called radicals, able to play the part of elements, and which unite with other simple bodies, or form among themselves double compounds. With the discovery of cyanogen, the theory of organic radicals received the first fact of the existence of compound bodies

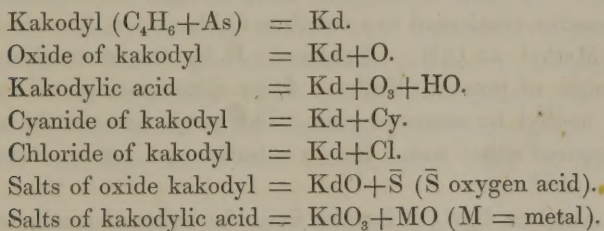
exhibiting the functions of an element. A radical combines with elements according to the common laws of inorganic chemistry, and may be replaced by another element.

But all radicals do not fulfil these conditions. The best criterion for considering a compound to be a radical is, that, when combinations with oxygen, sulphur, chlorine, &c. exist, this radical, under proper circumstances, can be transferred from one compound to the other.



Metals, such as iron, manganese, zinc, chromium, tin, antimony, arsenic, which enter into the composition of radicals, cannot be recognized by common reactions. An organic radical, like an element in inorganic chemistry, gives a foundation for a series of compounds.

The following table affords a view of a series of compounds of the radical Kakodyl, which can be prepared, partly direct, partly by substitution.



Inorganic chemistry may be defined as that branch of chemistry which treats of single radicals and compounds, in contradistinction to organic chemistry, which treats of compound radicals. Kakodyl and cyanogen were for a long time the only positive support of the radical theory; since the principal objection brought formerly against it was that the existence of a great many compounds had to be assumed, and were not known in an isolated state. But we may ask,



Could any one reasonably deny the existence of fluorine, although chemists succeeded only recently in isolating it from its compounds?

But this objection has been removed by the late important researches of Frankland and Kolbe, which proved beyond doubt the existence of the so-called alcohol-radicals, as ethyl, methyl, valyl, and amyl; and confirmed the theory — at least with regard to the composition of alcohol and ether — advanced more than seventeen years ago by Berzelius and Liebig. Löwig, Schweizer, and Landolt discovered still later a series of highly interesting radicals, which have a composition similar to the kakodyl of Bunsen, and enter into composition with elements in the manner of simple substances. The authors call them “stybethyl, ethyl-stibyl, stybmethyl.”

We will now, in succession, briefly describe the preparation and properties of these radicals.

Ethyl =  $C_4H_5$  = E. Prepared by the action of zinc on iodide of ethyl, in sealed tubes, at a temperature of  $150^\circ C$ .  $C_4H_5I + Zn = C_4H_5 + ZnI$ .<sup>\*</sup> Constitutes a colorless gas, without smell; at  $-18^\circ C$ . not yet liquified; by cold and pressure, condensed to a colorless fluid.

Methyl =  $C_2H_3$ . Prepared, 1, by the electrolyses of acetate of potassa (Kolbe); 2, by decomposition of iodide of methyl by means of zinc. The properties are the same, prepared either way. It is a colorless gas, not condensable at  $-18^\circ$ .

Amyl =  $C_{10}H_{11}$ . Results from the action of amalgamated zinc on iodide of amyl, above  $160^\circ C$ . Forms a transparent colorless liquid, of an ethereal odor and burning taste, not decomposed by potassium at  $155^\circ C$ .

Valyl =  $C_8H_9$ . Prepared by the action of a galvanic current on valerianic acid (Kolbe). Forms a colorless liquid of an ethereal odor. The formation of this radical from valerianic acid is explained thus:  $C_{10}H_{10}O_4 = C_8H_9 + 2CO_2 + H$ .

<sup>\*</sup> At the same time, two secondary products (methyl and clayl) are formed.



Frankland states the chemical character of the radicals ethyl, methyl, &c. to be as follows:—

1. They show the general deportment of hydrogen, but are less electropositive.

2. They are able to replace the hydrogen in any compound in which this element plays the part of a simple radical, and, when it does not occur in a group, where it displays the functions of a compound radical.

3. The haloid compounds of the named radicals may be considered as hydrogen acids, in which the hydrogen is replaced by one of these radicals.

4. They replace hydrogen in ammonia, as is shown in the alkaloids discovered by Wurtz and Hofmann, whereby the assumption of the hypothetical radical, amid, is useless.

5. They exhibit, besides the property of uniting with electro-negative elements, likewise that of combining with hydrogen.

Up to the present time, Frankland did not succeed in preparing the oxides of these radicals, as ether, &c.; these radicals namely show in general very indifferent chemical properties. This chemical indifference, when in an isolated state, is not surprising; they exhibit, in this respect, the same deportment as many elements (hydrogen, platinum), which combine with other bodies only when in *statu nascente*.

When the iodides of ethyl, methyl, &c. are decomposed by the action of zinc, arsenic, and phosphorus, ethyl, methyl, &c. will partly combine with those elements, whereby a number of new radicals are formed corresponding to kakodyl.

The existence of compounds of hydrogen with Ars, Sb, Te, as also the fact, that, in the new alkaloids of Wurtz, methyl and ethyl may be substituted for hydrogen, led Frankland to the conclusion, that, ere long, all the following compounds may be prepared. Those marked with \* have already been isolated.

Hydrogen Series.	Methyl Series.	Ethyl Series.	Butyryl Series.
HZn	$*(C_2H_3)Zn$	$(C_4H_5)Zn$	$(C_6H_7)Zn$
$H^2,As$	$*(C_2H_3)^2,As$	$(C_4H_5)^2,As$	$(C_6H_7)^2,As$
$*H^x,Sb$	$(C_2H_3)^x,Sb$	$(C_4H_5)^x,Sb$	$(C_6H_7)^x,Sb$
$*H^3,P$	$*(C_2H_3)^3,P$	$(C_4H_5)^3,P$	$(C_6H_7)^3,P$

Valyl Series.	Amyl Series.	Phenyl Series.
$(C_8H_9)Zn$	$*(C_{10}H_{11})Zn$	$(C_{12}H_5)Zn$
$(C_8H_9)^2,As$	$(C_{10}H_{11})^2,As$	$(C_{12}H_5)^2,As$
$(C_8H_9)^x,Sb$	$(C_{10}H_{11})^x,Sb$	$(C_{12}H_5)^x,Sb$
$(C_8H_9)^3,P$	$(C_{10}H_{11})^3,P$	$(C_{12}H_5)^3,P$

Stybethyl =  $(C_4H_5)^3,Sb$  (Löwig and Schweizer). It is prepared by the mutual decomposition of iodide of ethyl and antimoniuiret of potassium: forms a colorless liquid, of an onion-like odor. Its disposition to combine with other bodies is, with exception of potassium, kakodyl, and the haloides, unequalled. It unites, at a common temperature, with O, S, Se, Cl, &c., with evolution of heat. From its compounds it can, by means of potassium, again be separated, with all its original properties. One atom of stybethyl combines with two atoms of an element.

Under certain circumstances, two atoms of ethyl are dropped from stibethyl, and a new radical formed of the composition  $C_4H_5Sb$ , which has been called ethyl-stibyl, one atom of which unites with five atoms of an element. Löwig and Schweizer have succeeded in preparing compounds of bismuth and phosphorus similar to ethyl-stybethyl.

Stibmethyl =  $(C_2H_3)^3,Sb$ . Landolt, called upon by Löwig, isolated and examined stybmethyl. It is prepared by distilling iodide of methyl together with antimoniuiret of potassium. It is a liquid in every respect analogous to stybethyl. United with two atoms of oxygen, it constitutes a base satu-

rating two atoms of an acid, and forms also compounds with  $S_2$ ,  $Cl_2$ ,  $Br_2$ , &c.

Oxide of stibmethylium  $= (C_2H_3, Sb)O$ . — By pouring iodide of methyl into stibmethyl, Landolt received a crystallized compound of the formula  $(SbMe_4)I$ .  $Me = C_2H_3$ , which he calls iodide of stibmethylium. Its radical  $(SbMe_4)$ , not yet isolated, he gives the name of stibmethylium (analogous to ammonium).

The oxide of this radical  $(SbMe_4)O$ , which he isolated, is the more important, since its constitution confirms the ammonium theory of Berzelius. It occurs in white crystals. In its alkaline properties, it resembles most closely hydrate of potassa; is very corrosive; soluble in water and alcohol; attracts  $CO_2$  from the air, which is separated again by caustic lime. The aqueous solution of this body tests and smells like ley, feels soapy between the fingers, and evolves ammonia in the cold from the salts of ammonia. Lime, oxides of lead, mercury, copper, zinc, are at once precipitated; the last is redissolved in an excess: chloride of platinum yields a yellow precipitate. In a word, this compound body might, by simply qualitative reaction, be confounded with potassa: it forms with acids neutral and acid salts, resembling the corresponding potassa salts.

The investigations just mentioned are at a time when such contradictory views concerning the constitution of organic bodies are advanced, of the highest importance; and even the opposers of the radical theory will allow that of late it has gained considerable ground.

Although now perhaps most chemists agree with regard to the constitution of organic compounds, there is, however, still considerable arbitrariness respecting the composition of radicals.

Some, like Liebig and Wöhler, assume, besides binary radicals, consisting of C and H, ternary ones of CH and O; which latter Berzelius and Löwig reject. Berzelius, on the ground of his electro-chemical theory, denies, likewise, the existence of radicals containing Cl, Br, I; which scarcely



admits, now-a-days, of contradiction, as we will see hereafter. There are, also, probably radicals which contain S and Ph.

The following diagram will, with regard to the internal composition of oil of bitter almonds, exemplify how even advocates of the radical theory may be led to different conclusions.

*View of Ternary Radicals.*

Radical  $= C_{14}H_5O_2 = \text{Benzoyl.}$

Oil of bitter almonds  $= C_{14}H_5O_2 + H.$

Chloride of benzoyl  $= C_{14}H_5O_2 + Cl.$

Sulphuret of benzoyl  $= C_{14}H_5O_2 + S.$

*View of Binary Radicals.*

Radical  $= C_{14}H_6 = \text{Picramyl.}$

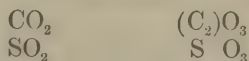
$(C_{14}H_6)O_2 = \text{oxide of picramyl.}$

$\left. \begin{matrix} C_{14}H_5 \\ Cl \end{matrix} \right\} + O_2 = \text{oxide of picramyl, in which one atom of chlorine replaces one atom of hydrogen.}$

$\left. \begin{matrix} C_{14}H_5 \\ S \end{matrix} \right\} + O_2 = \text{oxide of picramyl, in which one atom of sulphur replaces one atom of hydrogen.}$

Löwig believes in the existence of single radicals, for the following reason: oxalic acid, combined with oxide of lead, dried at  $100^\circ C.$  has the formula  $C_2O_3$ . Those chemists who consider this acid to be a higher oxide of carbon than carbonic oxide,  $= 2CO + O$ , render obvious the reason why it is so easily decomposed into CO and  $CO_2$ . But its strongly acid properties are not explained; besides, oxalic = rhodizonic = krokonic acid, belonging to one series, must then, although of organic origin, be ranked among inorganic acids; then oxides of carbonic oxide cannot be considered as organic bodies. To remedy this, Löwig assumes the existence of singular radicals, which consist of one or several atoms of one and the same element united as a whole by polar attraction. Oxalic acid contains, then, a radical  $(C_2)$ , = oxatyl,

combined with three atoms of oxygen, and stands now in the same relation to carbonic acid as sulphurous to sulphuric acid; thus:—



The radical theory was not enlarged by Liebig, but kept in its original limits. Berzelius extended it further, until, by the discovery of coupled compounds, he arrived at a new conclusion, namely, that the number of radicals was not very large, and deduced the apparently unlimited variety of combinations relative to organic bodies from the manifold proportion in which copulations may occur.

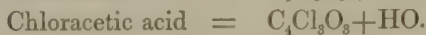
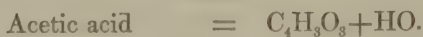
What is meant by coupled compounds we will illustrate by an example. Sulphovinate of baryta has the empirical formula,  $(\text{C}_4\text{H}_5)\text{O},\text{SO}_3 + \text{BaO},\text{SO}_3$ . Sulphovinate of baryta is soluble in water. In this and similar salts —  $(\text{C}_4\text{H}_5)\text{O},\text{SO}_3$  — is the copula, which adheres still to the liberated sulphuric acid by the separation of the base. By the addition of  $\text{SO}_3$  to the solution of sulphovinate of baryta, a precipitate of sulphate of baryta is formed, and again  $(\text{C}_4\text{H}_5)\text{O},\text{SO}_3 + \text{SO}_3,\text{HO}$ . This reaction proves, that, in the sulphovinate of baryta, there exists no ready-formed sulphate of baryta, but that it contains a coupled acid. The rational formula of sulphovinic acid is then  $\text{HO} + (\text{EO},\text{SO}_3),\text{SO}_3$ , when  $\text{E} = \text{C}_4\text{H}_5$ ; and for its salts ( $\text{M} = \text{metal}$ ),  $\text{MO} + (\text{EO},\text{SO}_3)\text{SO}_3$ .

Berzelius applied his theory of copulas likewise to organic bases (alkaloides), supposing their properties to be derived from ammonia ( $\text{NH}_3$ ), able to unite with organic compounds to copulas or coupled compounds.

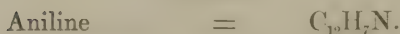
Dumas, who first defended zealously the radical theory, more lately advanced a new theory, called "*Theory of Substitution.*" Experiments of the effect of haloides on various organic compounds gave the result, that, from the latter, a part or all their hydrogen can be withdrawn, and Cl, Br, I, in the same atomical proportion be substituted, without the physical and chemical properties of the new compounds differing essentially from those of the original substance.

Organic acids retained their acid, — alkaloids their basic qualities; thus:—

*Acids.*



*Alkaloids.*

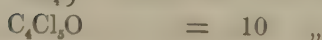
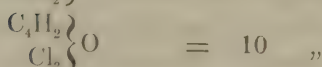
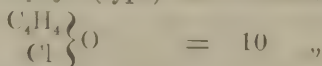
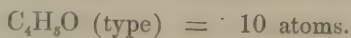


(Even compounds of  $\text{NO}_4$ ,  $\text{HIN}_2$ , have of late been substituted for H.)

Dumas, in speculating on these results, adopted the following view:—

Organic compounds are made up of a series of original groups of elements, in which every element may successively be replaced by another element (or compound), without the total group undergoing essential change in its original properties. These groups he calls “types” (primary forms). The chemical nature of the substitutes does not come into consideration when only the substitute replaces the elements in equivalents, and takes the same position in the group.

For the sake of an illustration, let us apply what has just been said to ether.





The doctrine of Dumas, strictly applied, leads to absurdities. Thus,  $C_4H_3O_3 + HO$  (acetic acid) = twelve atoms. By replacing all the elements by corresponding quantities of chlorine, we have,  $Cl_4 + Cl_3 + Cl_3 + Cl_2$  = twelve atoms. Such a compound, accordingly, should have the properties of acetic acid! Carbon is indispensable in organic compounds, and can never be replaced by other elements. A substitution of elements, therefore, must necessarily be limited to one element in binary, and to one or two in ternary, compounds, if the character of the original substance shall be retained at all.

Proceeding from the constitution of inorganic acids, the radical theory considers most organic acids to be hydrates, which, in combining with metallic oxides, lose one or several atoms of water.

The doctrine of types rejects absolutely the occurrence of ready-formed water in organic bodies in which substitutions take place. That such is the case is proved by the formation of chloracetic acid ( $C_4Cl_3O_3 + HO$ ), in which only three atoms of hydrogen can be replaced by chlorine, but not the fourth. The action of chlorine on acetic acid may be continued ever so long. The hydrate-water of this acid suffers no substitution, but only the hydrogen of the radical.

All dispute respecting the hydrate-theory seems to come to an end by Gerhardt's discovery of anhydrous acetic acid,  $= C_4H_3O_3$ , and benzoic acid,  $= C_{14}H_5O_3$ , which, able to take up water again, are transformed into the well-known hydrates of these acids. Deville, some time ago, discovered anhydrous nitric acid,  $NO_5$ .

Nevertheless, the theory of substitution accumulated many facts, which caused partly a remodelling of the original theory of radicals. We have to make a distinction between *primary* and *secondary radicals*, when all the phenomena of substitution find at once a satisfactory explanation. Organic radicals have, then, to be considered as a complex of atoms, able to undergo certain changes (substitutions), without suffering perceptible alterations in their chemical character,

so long as the molecular arrangement of the atoms remains stationary.

Possibly all the ternary radicals, containing O, S, Cl, &c. belong to the class of secondary (substituted) radicals. O, S, Cl (or even compounds, as  $\text{NO}_4$ ,  $\text{NH}_2$ , &c.), in taking the position of hydrogen-atoms, may assume more or less its functions.

Dumas's doctrine of types, although not yet strictly applied for a classification of organic compounds, gave occasion to so much doubt and arbitrariness, that Laurent introduced of late a new theory ("Nucleus Theory"), founded on the speculations of Dumas. It took root principally in France, until L. Gmelin adopted the same for classification in his celebrated Manual of Organic Chemistry. We will take a final view of this theory.

#### NUCLEUS THEORY.

Dumas's theory of types and substitution, which threatened to bring much confusion and arbitrary reasoning into the field of organic chemistry, served as the basis of a more scientific and better developed theory of the constitution of organic bodies. Starting from facts upon which the theory of substitution has been mainly built, Laurent brought to bear geometrical considerations on the arrangements of compound atoms. He conceived, *e. g.*, a geometrical figure, in which the solid angles were formed of carbon; the hydrogen ranging itself in such a manner between the atoms of carbon as to be in a state of chemical equilibrium, representing, in this respect, the equilibrium of gravitation in our planetary system. Those chemical systems of carbon and hydrogen in which an individual member cannot be removed without causing the whole structure to crumble and split into structures of a lower order, Laurent called nuclei or radicals. Those radicals or nuclei which contained only carbon and hydrogen he distinguished as "fundamental nuclei." To these belong, for instance,  $\text{C}_4\text{H}_4$ , ethene, and  $\text{C}_{20}\text{H}_8$ , naphthen.

It is clear, that, in a system of atoms in chemical equilibrium, as that above mentioned, an atom of hydrogen may be removed, and the system will still remain in equilibrium, provided the place of the atom of hydrogen removed be filled by an atom of another kind, however different this latter atom may be from the former in bulk and weight. The mutual attraction of the atoms, and their geometrical disposition, remain unchanged. Such systems, in which one or more atoms of hydrogen in the fundamental nucleus are homologically replaced by the same number of inorganic atoms, or organic compounds which behave like elementary substances, are designated by Laurent as "secondary or derived nuclei." The inorganic elements which generally replace H in fundamental nuclei are Cl, I, Br, O, N, and metals.  $\text{NO}_4$  = hyponitric acid,  $\text{NH}$  = imid,  $\text{NH}_2$  = amid,  $\text{NH}_3$  = ammonia,  $\text{C}_2\text{N}$  = cyanogen, are some of the compound bodies which are able to substitute H.

By removing, however, from the fundamental system or nucleus atoms of C, the original nucleus is destroyed, and one of a lower organization formed, in which the chemical equilibrium requires a different geometrical disposition of the atoms. The same change in geometrical disposition happens when H is removed without being replaced by an atom of a different body: the constitution of the nucleus is altered.

It is evident, from what has been said, that the relative position of the atoms, and their quantity, are of far more importance in this theory than their quality.

All derived nuclei present the same type, as they contain the same number of atoms of carbon in the same relative position to the other atoms as in the fundamental nucleus.

As the faces of cubes and octahedrons may serve as bases to pyramids, so the faces of systems of nuclei may serve as bases for the agglomeration of atoms of diverse elements. H, O, Cl, Br, I, and S, may in this way add themselves externally to the nucleus to form new types belonging to the series of the same fundamental nucleus. It is obvious that

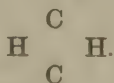


this theory aimed at explaining the chemical or rational constitution of organic bodies, as well as their crystallographic properties. No attempt, however, has been made yet to deduce the geometrical arrangement of the atoms, in the fundamental nuclei, from the crystalline form of organized bodies.

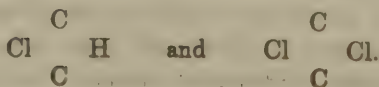
For an illustration, we will apply the nucleus-theory to explain the composition of acetic acid.

The primary nucleus of this acid is ethen,  $= C_2H_4$ : it has, perhaps, the form of a cube: four of the solid angles consist of four atoms of carbon; the four opposite ones, of four atoms of hydrogen. In the secondary nucleus,  $= C_2H_3O$ , one atom of oxygen has taken the position of one atom of hydrogen. On this oxygen-pole now collects one atom of hydrogen; and on the diametrically opposite carbon-pole, three atoms of oxygen. The formula of (hydrated) acetic acid is also  $O_3C_2H_3O, H$ ; i.e., three atoms of oxygen and one atom of hydrogen are placed without the secondary nucleus; and this theory Gmelin believes to be qualified for removing the radical theory as a mere fiction!

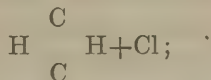
Elements or compounds which enter into the composition of primary nuclei cannot, without destruction of the compound, be qualitatively determined in the common way; but primary and secondary nuclei may, without change, unite with elements in such a manner that these do not enter into the figure of the nuclei, in which case they show the common behavior to reagents. For instance, the elements of a primary nucleus ( $C_2H_2$ ) may be thought to be arranged thus:—



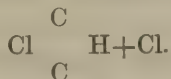
By the action of chlorine, two secondary nuclei may be formed,—



In these cases the chlorine cannot be recognized by nitrate of silver; but the primary nucleus may combine with chlorine, thus:—



or the secondary nucleus above,—



When the chlorine is placed without these nuclei, it will be precipitated by nitrate of silver.

This variable chemical deportment of one and the same element can readily be accounted for by the radical theory, thus: When chlorine enters into a radical as an integrant constituent, it is not recognizable as such by nitrate of silver, unless the radical type be destroyed; but when this element occurs in an organic compound, without entering into the composition of a radical, it shows the usual reactions.

Gerhardt and Laurent assume that one atom of an organic compound corresponds to four volumes of vapor: since then, in most cases, the elementary constituents of organic substances (C, H, Cl, Br, N, O, S, metal) present themselves in even numbers; but this statement is contradictory to many known facts. For instance, ether has the formula,  $\text{C}_4\text{H}_{10}\text{O}$  (compounds of acids and bases with ether, and the specific gravity of its vapor, entitle us to adopt this formula); and one atom of it is equal to two volumes of vapor. Gerhardt and Laurent, believing that one atom of ether-vapor corresponds to four volumes, assign to it the composition,  $\text{C}_8\text{H}_{20}\text{O}_2$ ; when we have even numbers of elementary atoms, but a wrong atomic weight.

Some acids, as oxalic,  $= \text{C}_2\text{O}_3 + \text{HO}$ , and krokonic acid,  $= \text{C}_3\text{O}_4 + \text{HO}$ , &c., form likewise exceptions to these laws. Gerhardt and Laurent double these formulæ to make the number of atoms of each constituent divisible by two. Cya-

nogen only, the principal representative of organic radicals, could not be subjected to these laws.

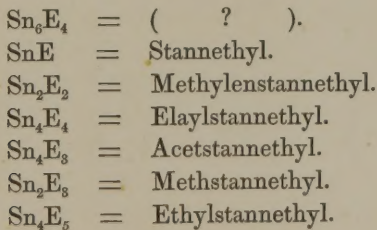
These chemists, who went so far as to apply their hypothetical laws of organic nature to inorganic bodies, have caused great confusion in the science of chemistry.

The radical theory, although still in its progression, seems, in spite of all its deficiencies, to be more appropriate than any of the others to bring clearness and order into the classification of organic compounds, and to give a satisfactory explanation of all positive facts. In conclusion, it is believed that the attempt of some French chemists to overthrow the radical theory can by no means be considered a successful one.

## A P P E N D I X.

SINCE the writing of this article, C. Löwig published "Chemisch-Pharmaceutisches Central-Blatt," 1852, Nos. 50, 55, and 56; a series of new investigations on Organic Radicals.

This author, as we have stated, found previously, that, by the action of iodide of ethyl, iodide of methyl, &c. on alloys of antimony, arsenic, bismuth, with potassium, these metals unite with ethyl, methyl, amyl, in the same proportion as they do with hydrogen, and form compounds which, in their chemical relation and composition, correspond to ammonia and ammonium. He now submitted alloys of tin (and lead) with sodium, to the action of iodide of ethyl. These new radicals unite directly and violently with oxygen and the haloids; their oxides are very strong bases, and precipitate metallic oxides; with acids they produce crystalline salts. The radicals have the following formulæ:—



These radicals correspond, with exception of the first two, to well-known organic radicals, containing carbon and hydro-



gen; carbon in the place of tin, and hydrogen in lieu of ethyl. By these substitutions, we have —

Metylen	=	$C_2H_2$ .
Elayl	=	$C_4H_4$ .
Acetyl	=	$C_4H_3$ .
Methyl	=	$C_2H_3$ .
Ethyl	=	$C_4H_5$ .

The result of this interesting research is, that, whilst antimony, bismuth, &c. are closely allied to nitrogen in their deportment to organic radicals, tin and lead give compounds in which these metals take the part of carbon; since several atoms of them unite with ethyl, methyl, &c. forming compounds corresponding to the formula,  $Sn_4E_3$ ,  $Sn_4E_3$ .

The radicals have the following formulae: —

$Sn_4E_3$	=	Stannyl
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These radicals correspond with exception of the first two to well known organic radicals containing carbon and hydrogen.

